Journal of Physics: Conference Series **114** (2008) 012048 doi:10.1088/1742-6596/114/1/012048

Effect of Substrate Temperature on Structural Properties of Thermally Evaporated ZnSe Thin Films of Different Thickness

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Abstract. The ZnSe, a wide band gap semiconductor has high potential for application in optoelctronic applications. The structural parameters of a thin film semiconductor largely depend on the preparation method and conditions. Transparent ZnSe thin films of thickness 200-450nm have been prepared by thermal evaporation method on chemically cleaned glass substrates at different substrate temperatures from room temperature to 523K. The film structure was studied by x-ray diffraction technique and different micro structural parameters were determined from it. The XRD spectra showed that the ZnSe films prepared at higher substrate temperature are polycrystalline in nature and have a cubic (zinc-blende) structure. The average grain size of the polycrystalline ZnSe films calculated from XRD line spectra using Scherrer’s formula was found to increase from 13nm to 33nm with increase of substrate temperature from 373K to 523K. . The internal strain and dislocation density of these films were found to decrease with increase of substrate temperature and also with thickness.

1. Introduction

ZnSe(Zinc-Selenide), a direct gap II-VI semiconductor with band gap energy of 2.67 eV, has long been found as promising material for optoelectronic devices such as LED, thin film transistor, blue laser diode etc [1-3]. Because of its large band gap, ZnSe has been used as window layer for the fabrication of photovoltaic solar cells. There are a number of reports on the different structural, optical and electrical properties of ZnSe polycrystalline thin films prepared by various techniques such as chemical vapour deposition, MOCVD, Electrodeposition, Photochemical deposition, chemical bath deposition(CBD), pulsed laser deposition and thermal evaporation [4-12]. It is seen that different parameters of a film are structural dependent which is also depends on the method of preparation, its thickness and other factors. The thermal evaporation method is cost effective and suitable for large area deposition. We have prepared the ZnSe thin films of different thickness by thermal evaporation method at different substrate temperatures. The different structural parameters of these films were determined and the effect of substrate temperature is studied in this paper.

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2. Experimental

The ZnSe films were prepared by vacuum evaporation method under the pressure better than 10^{-5} Torr on chemically cleaned glass substrates from 99.99% pure ZnSe powder (Aldrich) using molybdenum boat. The substrates were kept a distance 8 cm from the material boat. The ZnSe films of different thicknesses in the range 2000–4500 Å were deposited at a nearly same deposition rate. The substrate temperature was maintained at 373 to 573 K. The thickness of all the films was measured by multiple beam interferometer (MBI) technique. The X-ray diffraction pattern of the films were studied by the Bruker X-ray diffractometer. The structure of the films was analyzed by an X-ray diffractometer (using CuK_α) radiation with wave length (λ) 1.5406 Å in the 2θ range from 10^0 to 70^0.

The crystallite size (D) were calculated using the Scherrer's formula [13] from the full-width at half-maximum (FWHM) (β):

$$D=k\lambda/ \beta \cos\theta$$

The micro strain (ε) was calculated from formula [14]

$$\varepsilon= \beta \cot\theta/4$$

The dislocation density (δ), defined as the length of dislocation lines per unit volume of the crystal, was evaluated from the formula for the (1 1 1) plane [15]

$$\delta=15\varepsilon/aD$$

The lattice parameter 'a' can be evaluated from the relation

$$a=d(h^2+k^2+l^2)$$

where h, k, l are Miller indices.

From the calculated value of lattice constant for different planes we have drawn Nelson–Riley plots [16] (Fig. 3) with the error function $f(\theta)=1/2(\cos^2\theta/\sin \theta +\cos^2 \theta / \theta)$. The intercept of this plot gives the corrected value of lattice constant.

3. Results and discussions

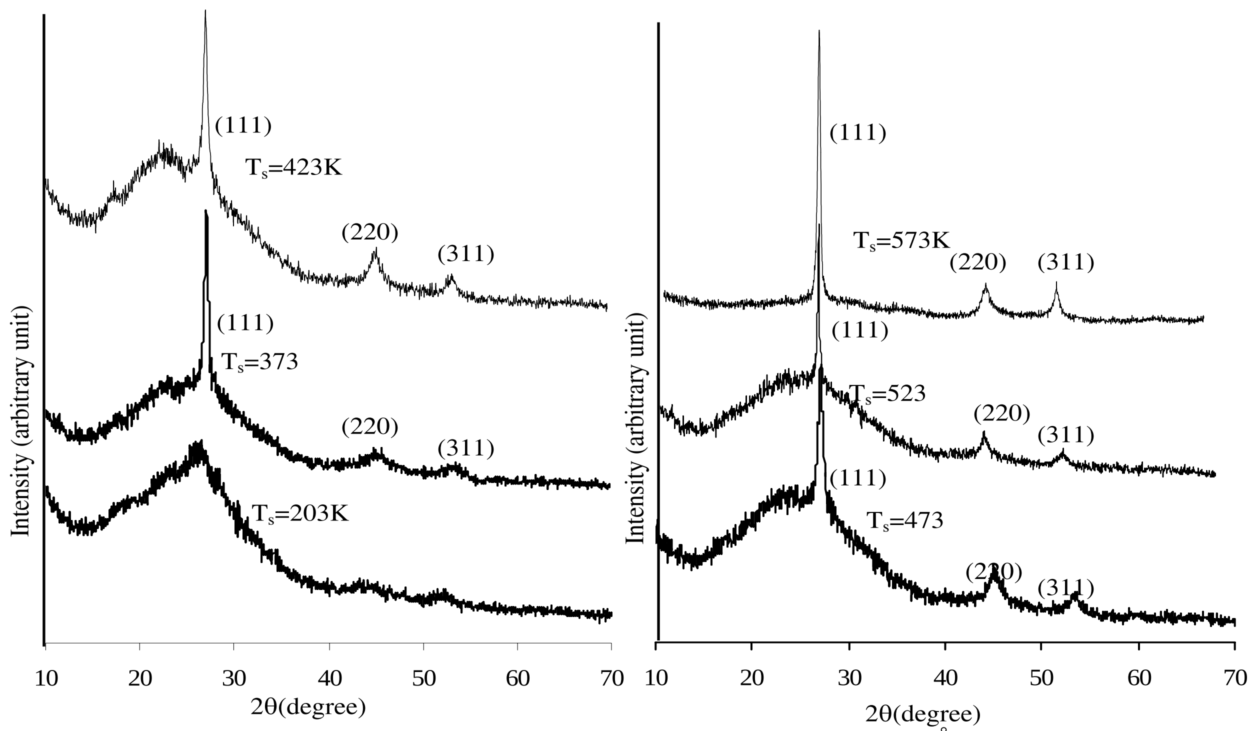

Figure 1: XRD spectra of six typical ZnSe films of thickness about 3000 Å thermally deposited at different substrate temperatures (T_s)

X-ray diffractograms of the ZnSe films of thickness in the range of 2800 to 3200(Å) deposited at different substrate temperatures are shown in the Figure 1. From the XRD pattern it is found that the ZnSe films prepared at higher substrate temperature are polycrystalline however the film prepared at room temperature is amorphous in nature. The main features of the diffraction pattern are the same but only the peak intensity is varied. The films with lower thickness, the X-ray diffraction spectrum shows almost featureless spectra with very weak peaks. The peak intensity increases with increasing film thickness. The diffraction spectra display the characteristics diffraction peaks of the cubic phase of ZnSe [16]. Three prominent diffraction peaks were observed at 2θ values at 27.224, 45.23 and 53.649 degree corresponding to (111), (220) and (311) planes of this phase respectively and indicate random orientation of crystallites in these films [17]. However, in all cases the intensities of the (2 2 0) and (3 1 1) peaks were extremely low in comparison with the (1 1 1) one. This indicates a preferential orientation of the micro-crystallites with the (1 1 1) direction perpendicular to the substrate. The [111] is the close packing direction of zinc blende structure. It is also observed that with increasing T_s, the peak intensity (counts/sec) also increases and the peaks become sharper indicating larger crystallite size D at elevated substrate temperature. As no other peak with measurable intensity from either ZnSe or the constituent was obtained in the x-ray diffractogram, so it indicates the formation of polycrystalline film with zinc blende structure. From these results it can be concluded that the elevated substrate temperatures (373K to 573K) are the suitable optimum growth conditions to prepare good quality polycrystalline thin films. As the film thickness increases, the diffraction intensity increases due to the growth of the materials incorporated in the diffraction process [18].

The lattice constant of all the ZnSe thin films of different thicknesses (t) prepared at different substrate temperatures on glass substrates are calculated by using the relevant formula and are found slightly different values for different orientations of the same film. From the calculated values of lattice constants we have drawn Nelson–Riley plots (Figure 2) with error function and the correct values of lattice constants are estimated and are tabulated in Table 1. The variation of lattice constant (corrected) with substrate temperature is shown in figure 3. Form the plot it is seen that the lattice constant first increases with substrate temperature and reaches nearer to the value of lattice constant of bulk ZnSe (5.667 Å) at substrate temperature in between 500K and 523K then shows a decreasing tendency.

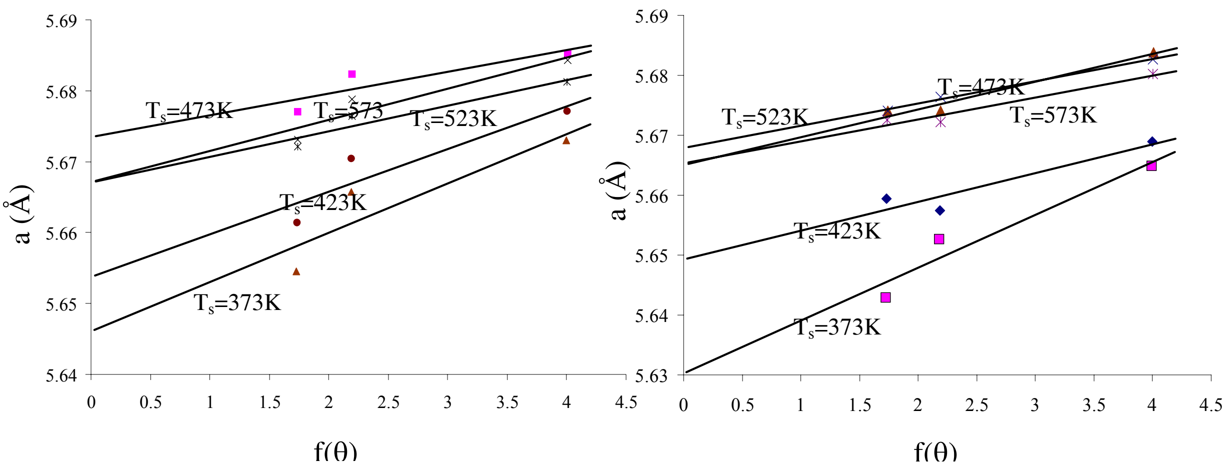

Figure 2. Nelson-Riley plots for calculation of corrected value of lattice constant of ZnSe films deposited at different substrate temperatures of thickness (a) about 2100Å and (b) about 3000 Å

The FWHM was found to decrease markedly with film thickness and substrate temperature to 573K. Such a decrease reflects the decrease in the concentration of lattice imperfections due to the decrease in the internal micro-strain within the films and an increase in the crystallite size [18]. Table1

shows a comparative look of grain size, internal stress, internal strain and dislocation density of the ZnSe thin films of different thicknesses prepared at different substrate temperatures on glass substrates. It is observed that the crystallite size increases but the internal strain and dislocation density decreases with increase of film thickness and substrate temperature on glass substrates. When thickness increases the average grain size increases and for the film with higher thicknesses the size of the grains does not increase considerably. Since the dislocation density and strain are the manifestation of dislocation network in the films, the decrease in the strain and dislocation density indicates the formation of higher quality films at higher substrate temperatures. When the substrate temperature increases the line width narrows due to the increase in crystallite size. The adatom mobility also increases as the substrate temperature increases which also results in the crystalline size and crystallinity of the films [19].

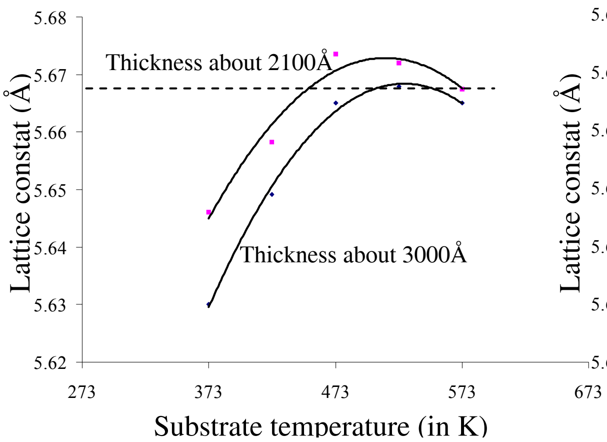

Figure 3. Variation of lattice constant (corrected) with substrate temperature of ZnSe films of different thickness

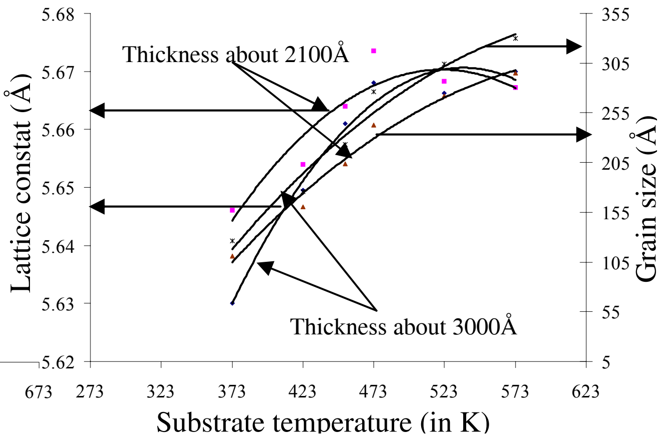

Figure 4. Variation of lattice constant and grain size with substrate temperature of ZnSe films of different thickness for [111]

A stress is also developed in all vacuum deposited film due to the lattice misfit with the substrate. However, the stress has two components: thermal stress arising from the difference of expansion coefficient of the film and substrate and internal stress due to the accumulating effect of the crystallographic flaws that are built into the film during deposition. The average stresses of the deposited films are found to be compressional in nature. The compressive stress is due to the grain boundary effect, which is predominant in polycrystalline film [20]. Native imperfections probably migrate parallel to the film substrate with their surface mobility modified by the substrate temperatures. All the evaporated ZnSe films coated at room temperature (303 K) are found to be dominated by internal stress rather than thermal stress.

4. Conclusion

ZnSe thin films of different thickness have been prepared by thermal evaporation method at different substrate temperatures and the structural parameters such as crystalline size, lattice constant, stress, strain and dislocation density were calculated. From the XRD spectra it is found that the ZnSe films prepared at higher substrate temperature are polycrystalline in nature and have a cubic (zinc-blende) structure. With the increase of substrate temperature the average grain size of the films is found to be increased, however the internal strain and dislocation density decreased. Good quality polycrystalline thin films of ZnSe can be prepared at a substrate temperature nearer to 523K, at which the lattice constant is found to be nearer the value of bulk ZnSe.

Table1: Microstructural parameters of thermally evaporated ZnSe thin films of different thickness on glass substrate prepared at different substrate temperatures

Substrate temp K	Thickness in (Å)	Plane [hkl]	Lattice constant (Å)	Corrected Lattice const (Å)	Grain Size (Å)	Internal stress in $10^8 N/m^2$	Internal strain 10^{-2}	Dislocation density 10^{11} line/cm^2
373	2000	[111] [220] [311]	5.673 5.6657 5.6545	5.646	111	4.532	1.46	34.78
	2800	[111] [220] [311]	5.665 5.653 5.643	5.63	127	7.986	1.28	26.72
423	2100	[111] [220] [311]	5.677 5.670 5.661	5.6583	160	1.878	1.01	16.685
	3100	[111] [220] [311]	5.669 5.657 5.659	5.65	173	3.842	0.94	14.332
473	1900	[111] [220] [311]	5.685 5.682 5.677	5.6735	243	-1.166	0.669	7.259
	3200	[111] [220] [311]	5.684 5.674 5.674	5.665	270	0.432	0.594	5.74
523	1800	[111] [220] [311]	5.684 5.678 5.673	5.672	272	-1.08	0.598	5.809
	2900	[111] [220] [311]	5.682 5.676 5.674	5.668	306	-0.194	0.529	4.55
573	2200	[111] [220] [311]	5.881 5.676 5.672	5.6675	295	-0.108	0.55	4.932
	3000	[111] [220] [311]	5.68 5.672 5.672	5.665	332	0.432	0.489	3.894

Acknowledgement
The authors sincerely thank Dr Monoranjan Kar, Scietific Officer, Nanotechnology Centre, IIT Guwahati, for providing the XRD facility. Two of the authors (S C and M N B) are also thankful to the UGC of India for granting Teachers Fellowship for these research works.

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